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(54) [Title of the Invention] Production of Silicon Single Crystal

(57) Summary

[Object] The object of the present invention is to provide a method for production of silicon single crystal that has excellent oxide layer breakdown voltage characteristics, etc. by reduction of density of oxide precipitates across the wafer surface.

[Composition] The present invention is a method for production of silicon single crystal by the Czochralski method comprising maintaining of a coefficient expressed as fp/G at a value of 0.25 $mm^2/°C$ (fp (mm/mm) = crystal growth rate, G (°C/mm) = crystal axial direction temperature gradient in the temperature range of silicon melting point to 1300°C), and carrying out crystal growth while cooling at a rate of 2.0°C/min. or less over the temperature range of 1150°C to 1000°C.

[Scope of the Patent Claims]

[Claim 1] A method for production of silicon single crystal by the Czochralski method comprising maintaining of a coefficient expressed as fp/G at a value of 0.25 $mm^2/°C$ (fp (mm/mm) = crystal growth rate, G (°C/mm) = crystal axial direction temperature gradient in the temperature range of silicon melting point to 1300°C), and carrying out crystal growth while cooling at a rate of 2.0°C/min. or less over the temperature range of 1150°C to 1000°C.

[Detailed Explanation of the Invention]

[0001]

[Industrial Field of Use] The present invention relates to a method for production of silicon single crystal, particularly for silicon single crystal produced by the Czochralski method, so that crystal quality (e.g., oxide layer breakdown voltage, etc.) is excellent.

[0002]

[Earlier Technology] Although there exist various types of production methods for silicon single crystal used for LSI material, the Czochralski method (referred to hereinafter as the CZ method) has been mainly adopted as a method capable of industrial volume production.

[0003] Figure 3 is a simplified cross-sectional drawing showing conditions of this CZ method. Within this figure, item 1 is a crucible which has a double structure comprising an interior quartz crucible 1a and an exterior graphite crucible 1b. A heater 2 is disposed to the exterior of crucible 1. Crucible 1 contains crystal growth material melted by this heater to form silicon melt 4. The tip of a seed crystal 3 attached to the tip of a pull shaft or cable is made to contact the surface of this melt 4, and this seed crystal 3 is pulled up while the crucible and seed crystal are made to rotate, thereby causing single crystal 5 to grow at a certain growth rate by freezing of melt 4 at the bottom tip of the seed crystal. Normally the utilized growth rate is 1.0 to 2.0 mm/min.

[0004] During pulling, an oxygen component dissolved from the quartz crucible into the silicon melt becomes incorporated into the crystal. Therefore supersaturated oxygen is frozen within the lattice of the pulled silicon single crystal. These supersaturated frozen interstitial oxygen atoms generate defects caused by oxygen (e.g., oxygen precipitates, oxygen induced stacking faults, dislocations, etc.) during LSI production processing, particularly during thermal oxidation steps. Device characteristics are markedly lowered when such defects occur in the active region of the device.

[0005] In recent years, gate oxide layer thinning has progressed in accompaniment with an increased degree of integration of MOS devices. There is strong demand for improvement of gate oxide layer reliability (i.e., oxide layer breakdown voltage characteristics). However, silicon single crystal wafers manufactured by the CZ method, in comparison to wafers grown by the float zone method (referred to hereinafter as the FZ method), have markedly worse reliability of the gate oxide layer. For example, when oxygen precipitates within the silicon single crystal, which appear to be the cause of worsening of oxide layer breakdown voltage characteristics, are measured by the infrared scattering tomography method, density of such oxide precipitates in silicon single crystal produced by the CZ method is about 10^6 cm^{-3}, which is a comparatively high density of oxygen precipitates in comparison to a wafer grown by the epitaxial method or single crystal grown by the FZ method.

[0006] A strong relationship is apparent between the density of oxygen precipitates observed immediately after single crystal growth and MOS device oxide layer breakdown voltage characteristics. Oxide layer breakdown voltage characteristics can be improved by lowering density of oxygen precipitates. However, grown oxygen precipitates are extremely stable during crystal growth, and causing such oxygen precipitates to disappear at the thermal oxidation temperatures normally used during LSI manufacturing processing (1250°C or less) is difficult. When such oxygen precipitates are generated in the active region of a semiconductor device, not only does reliability of the gate oxide layer decline, but also element characteristics decline due to worsening of junction leakage characteristics.

[0007] When silicon single crystal is pulled at a certain growth rate (0.8 mm/min.) or greater, a ring of oxygen induced stacking faults (referred to hereinafter as the OSF ring) may be generated across the wafer surface by carrying out thermal oxidation treatment after processing of the silicon single crystal into wafers. Since the OSF ring is generated at a region separated from the active region of the wafer surface, the OSF ring itself normally has no effect upon manufacturing processing. However, highly thermally stable oxygen precipitates are distributed at a high density of about 10^6 cm^{-3} across the interior region of this OSF ring (although oxygen precipitates don't exist in the region exterior to the OSF ring). Therefore there have been problems such as lowering of gate oxide layer reliability and lowering of junction leakage characteristics.

[0008] A method previously proposed for control of the density of oxygen precipitates within the silicon single crystal pulled by the CZ method is growth of the single crystal at a low rate of 0.8 mm/min. or less (e.g., see Publication of Unexamined Patent Application No. Hei 2-267195).

[0009] The inventors of the present invention, confirmed that adoption of this type of low crystal growth rate was capable of preventing the existence of oxygen precipitates in the single crystal or capable of extreme lowering the density of such oxygen precipitates, thereby making possible a great improvement of oxide layer breakdown voltage characteristics.

[0010] However, the growth rate of single crystal means the pulling velocity of silicon single crystal, which is directly tied to the production rate of silicon single crystal. Generally a value of 1.0 mm/min. or greater is adopted as the pull rate during industrial production of silicon single crystal as explained above. A slowing pull rate as per the above mentioned method would result in greatly lowered silicon single crystal productivity.

[0011] When growth rate is the silicon single is lowered (i.e., to 0.8 to 0.6 mm/min.), and wafer quality is examined, the OSF ring may be generated at the center of the wafer surface, and oxygen precipitate density within the OSF ring internal region of the wafer surface may be found to rise to a density of about 10^4 cm^{-3}. As the growth rate is lowered further (e.g., 0.6 mm/min. or less), although an OSF ring isn't generated across the wafer surface, dislocation clusters are newly generated at a density of about 10^3 cm^{-2}, and intrinsic gettering capability, an excellent property of silicon single crystal produced by the CZ method, markedly worsens.

[0012] Although gate oxide layer reliability increases when silicon single crystal of such quality is used for the manufacture of LSI, a problem results of overall lowering of reliability of the semiconductor element due to generation of dislocation clusters and marked lowering of intrinsic gettering capability.

[0013]

[Problems to be Solved by the Invention] The object of the present invention is to solve the above mentioned problems of silicon single crystal production technology by establishing a method for production of silicon single crystal that has excellent crystal quality (e.g., oxide layer breakdown voltage characteristics, etc.) by lowering of the density across the wafer surface of oxygen precipitates.

[0014]

[Means to Solve the Problems] The inventors of the present invention paid attention to oxygen precipitates within silicon single crystal observed immediately after crystal growth, formation of OSF nuclei, as well as cooling rate and temperature distribution of the pulled silicon single crystal as a means for controlling such precipitates and OSF nuclei.

[0015] As a result, it was discovered during the silicon single crystal production step that by maintaining of a fixed relationship expressed as fp/G at a value of 0.25 $mm^2/°C$ (fp (mm/mm) = crystal growth rate, G = crystal axial direction temperature gradient (°C/mm) in the temperature range of the silicon melting point (1410°C to 1414°C) to 1300°C), the OSF ring generated by post-wafer-processing thermal oxidation treatment could be distributed at the perimeter of the wafer in a region unused for LSI manufacture, and by carrying out crystal growth while controlling cooling rate, oxygen precipitates within the crystal could have the low density of 10^5 cm^{-3}.

[0016] The below mentioned silicon single crystal production method was accomplished based upon such knowledge.

[0017] That is to say, the present invention is a method for production of silicon single crystal by the Czochralski method comprising maintaining of a coefficient expressed as fp/G at a value of 0.25 $mm^2/°C$ (fp (mm/mm) = crystal growth rate, G (°C/mm) = crystal axial direction temperature gradient in the temperature range of silicon melting point to 1300°C), and carrying out crystal growth while cooling at a rate of 2.0°C/min. or less over the temperature range of 1150°C to 1000°C.

[0018] Here the temperature gradient (°C/mm), in the same manner as cooling rate, is the speed of crystal cooling and indicates cooling temperature (°C) per unit length (1 mm) of crystal.

[0019] Figure 1 is a drawing that shows schematically the relationship of the interface between melt 4 and pulled single crystal 5. Within this figure, x0 is the point of the crystal where freezing starts at the interface along the crystal axis (i.e., x-x axis). Here x1 is the crystal position along the x-x axis which indicates distance from the interface (or distance from the bottom of the crystal). Therefore if x1 is taken to be the position where the crystal is at 1300°C, the above mentioned temperature gradient G becomes (1410°C - 1300°C) / (distance from x0 to x1 in mm units).

[0020]

[Operation of the Invention] The inventors of the present invention utilized crystal growth devices (4 types) for the CZ method that differed in device dimensions and production conditions such as growth rate, temperature gradient, etc. The relationship between rate of single crystal growth and temperature gradient within the crystal and generation of the OSF ring by thermal oxidation treatment after wafer processing were examined. These examination results are summarized below.

[0021] (1) When crystal production devices were used under identical conditions, exterior diameter of the OSF ring generated in the wafer depended upon crystal growth rate. Exterior diameter of the generated OSF ring decreased as crystal growth as carried out at low speed. However, when a crystal growth device was used that had different conditions, even at the same growth rate, exterior diameter of the OSF ring generated within the wafer varied.

[0022] (2) Even when crystal growth devices are used that have different conditions, the exterior diameter of the OSF ring generated in the wafer can be controlled if the temperature gradient along the crystal axis direction over the temperature range of the silicon melting point to about 1300°C is controlled in addition to single crystal growth rate. That is to say, exterior diameter of the generated OSF ring can be chiefly determined by control of the relationship expressed as fp/G ($mm^2/°C$ units; fp (mm/mm) = crystal growth rate; G (°C/mm) = crystal axial direction temperature gradient in the temperature range of silicon melting point to 1300°C).

[0023] Figure 2 shows the relationship between exterior diameter of the OSF ring generated in the wafer (mm) and the crystal growth rate (fp = mm/min.). Also Figure 3 shows the relationship between OSF ring exterior diameter (mm) and the coefficient ($fp/G = mm^2/°C \cdot mm$) indicating single crystal growth rate (fp = mm/min.) and temperature gradient (°C/mm) along the crystal axial direction in the temperature range of the silicon melting point to 1300°C.

[0024] Four types of devices (production devices 1 through 4) were used for Figure 2 and Figure 3. Although these respective devices were manufacturing devices using the CZ method, single crystal production conditions varied due to differences in construction. However, a 16" diameter quartz crucible was placed in each manufacturing device, and 36 kg of high purity polysilicon was charged into the crucible as precursor melt material. The charge was boron doped, and the polysilicon was melted by heating. Thereafter a 150 mm diameter <100> crystal growth orientation silicon single crystal was grown to a length of 700 mm (i.e., tested single crystal at positions from the bottom ranging from 200 mm to 500 mm). Thereafter a total of 12 single crystal ingots were produced at single crystal growth rates of 0.4, 0.65, 0.75, and 0.95 mm/min. (maximum pulling rate for the various manufacturing devices).

[0025] As is made clear by Figure 2, for each of the manufacturing devices, the generation position of the OSF ring changed from the wafer perimeter region to the center as crystal growth rate decreased, and the generated OSF ring exterior diameter became small. However, depending upon the manufacturing device, exterior diameter of the generated OSF ring varied even when crystal growth rate was the same.

[0026] As shown in Figure 3, when the coefficient expressed as fp/G, between the crystal growth rate during single crystal pulling (fp = mm/min.) and the temperature gradient (G = °C/m) along the crystal axis direction, had a value of 0.25 $mm^2/°C \cdot min$ or less, even after thermal oxidation treatment of the processed wafer, almost no OSF ring was seen to be generated. However, when the coefficient (fp/G) was in the range of 0.22 to 0.25 $mm^2/°C \cdot min$, an OSF ring was generated in the central region of the wafer surface (region of 15 to 60 mm radius from the center). [*TRANSLATOR'S NOTE: "G = °C/m" here and later looks like an error in the source text since the length is expressed elsewhere in mm units.*]

[0027] By treatment according to the coefficient (fp/G) relating crystal growth rate (fp) and crystal axial direction temperature gradient (G), generation position of the OSF ring can be largely determined independently of the manufacturing device.

[0028] The method of the present invention sets pulling conditions such that the coefficient (fp/G) has a value of at least 0.25 $mm^2/°C \cdot min$ and grows single crystal such that the OSF ring generated by thermal oxidation is caused to be generated at the perimeter region of the wafer surface.

[0029] Furthermore, the inventors of the present invention, as a result of additional detailed investigations related to formation and growth of nuclei of oxygen precipitates formed during crystal growth, observed that point defects formed during silicon single crystal growth, particularly by use of the effects of vacancies, were capable of controlling the density, etc. of oxygen precipitates.

[0030] Generation of oxygen precipitates during silicon single crystal growth progresses according to the reaction indicated by the following equation (A).

[0031]

$$(1 + z)\,Si + 2Oi + 2yV = SiO_2 + zI \quad .... \quad (A)$$

Here, Si is a lattice silicon atom, Oi is an oxygen atom interstitial, V is a vacancy, I is an interstitial silicon atom, SiO_2 is an oxygen precipitate, y is a coefficient indicating the proportion of vacancies absorbed due to growth of the oxygen precipitate, and z is a coefficient indicating the proportion of interstitial silicon atoms ejected by growth of the oxygen precipitate. Then the free energy $-\Delta G$ of formation of the oxygen precipitate is shown by equation (B) below. However, for simplification, contribution of interstitial silicon and the contribution of distortion in accompaniment with growth of precipitates is not considered here.

[0032]

$$\Delta G = -n(r)\,KT\,\ln(Co/Co^*) - yn(r)\,KT\,\ln(Cv/Cv^*) + 4\pi r2\sigma \quad .... \quad (B)$$

Here, n(r) is the number of oxygen atoms within an oxygen precipitate of radius r, K is the Boltzmann constant, T is temperature, Co is the oxygen concentration, Co* is the thermal equilibrium concentration of oxygen, Cv is the concentration of vacancies, Cv* is the thermal equilibrium concentration of vacancies, and σ is the interfacial energy of the oxygen precipitate. From equation (B), when the vacancy concentration Cv is lower than the thermal equilibrium concentration Cv*, the second term {yn(r) KT ln (Cv/Cv*)} becomes positive, and the energy barrier for nuclei formation is increased. Therefore nuclei formation becomes difficult. On the other hand, when the concentration of vacancies is in excess of the thermal equilibrium value Cv*, the second term {yn(r) KT ln (Cv/Cv*)}becomes negative, and the energy barrier is lowered so that nuclei formation readily progresses. As a result of experiments of the inventors of the present invention, oxygen precipitation becomes possible at a relative temperature of about 1150°C. Moreover, when crystal temperature drops in accompaniment with pulling of single crystal, since the oxygen and vacancy thermal equilibrium concentrations Co* and Cv* become lower, the energy barrier quickly declines further. Therefore further oxygen precipitates are readily formed within the crystal.

[0033] When the concentration Cv of vacancies is in excess of the concentration Cv* at thermal equilibrium during excessive cooling of the single crystal in the temperature region of 1150°C to 1000°C, nuclei can be formed in this temperature region. Since the crystal is at high temperature when nuclei are formed, the rate of oxygen precipitate growth becomes large. However, since vacancies are absorbed and disappear in accompaniment with the growth of precipitates, the concentration of vacancies Cv within the crystal begins to drop. Therefore the second term {yn(r) KT ln (Cv/Cv*)}of equation (B) gradually increases so that the energy barrier for nuclei formation increases as precipitation progresses, and precipitate formation again begins to be suppressed.

[0034] Therefore, when the concentration Cv of vacancies within the crystal is fixed and in excess of the thermal equilibrium concentration Cv* at the temperature of initiation of precipitation (vicinity of 1150°C), the size and density of the formed oxygen precipitates (referred to hereinafter as the size) become dependent upon the rate of cooling of the single crystal in the temperature range of 1150°C to 1000°C (or the time period of the crystal in the temperature range of 1150°C to 1000°C). That is to say, when the rate of cooling within this temperature range is lowered, the time period that the crystal exists in this temperature range is prolonged so that growth of oxygen precipitates is stimulated and size increases. Moreover, since the concentration Cv of vacancies drops in accompaniment with growth of oxygen precipitates, precipitate nuclei formation is suppressed, and therefore the density of subsequently generated oxygen precipitates drops.

[0035] Next, the capability to control of density distribution an size of oxygen precipitates in the single crystal by adjustment of the rate of cooling over the temperature range of 1150°C to 1000°C will be explained based upon experimental data.

[0036] The silicon single crystal production method used for these experiments was nearly the same as that used for Figure 2 and Figure 3. After 50 kg of high purity polysilicon was charged into a 16" diameter quartz crucible, the charge was doped with boron, and the polysilicon was melted by heating. A 130 mm diameter silicon single crystal of <100> crystal growth orientation was pulled to a length of 800 mm.

[0037] In order to adjust cooling rate, during pulling when the length of single crystal reached 300 mm, growth rate of the crystal (pull rate) was changed from 1.1 mm/min. to 0.5 mm/min. Again when single crystal length reached 450 mm, growth rate during crystal production was changed from 0.5 mm/min. to 1.1 mm/min. In this manner, by carrying out pulling while changing growth rate, it became possible to continuously vary cooling rate of the silicon single crystal at positions along the crystal axial direction.

[0038] The silicon single crystal produced in this manner was processed into wafers. These wafers were mirror polished, and then oxygen precipitate density and size were determined at the wafer central region by infrared scattering tomography.

[0039] Figure 4 is a drawing showing cooling rate and the results of measurements by infrared scattering tomography. Figure 4 (a) shows density of oxygen precipitates. Figure 4 (b) shows the square root of scattering intensity of oxygen precipitates. Here since the value of the square root of scattering intensity is thought to be inversely proportional to the volume of oxygen precipitates (the scatterer), this indicates the size of the oxygen precipitates. Furthermore, Figure 4 (c) shows results of actual measurements of cooling rate in the temperature range of 1150°C to 1000°C at the respective crystal positions.

[0040] As is made clear by Figure 4 (a), cooling rate became 1.1 °C/min. in the crystal position range of 180 mm to 255 mm, where the density of oxygen precipitates became about 10^5 cm^{-3}, which was quite low in comparison other ranges. As cooling rate was increased at other crystal positions, density of oxygen precipitates gradually increased, rising to a density of 10^6 cm^{-3} when cooling rate exceeded 2.0°C/min.

[0041] The square root of scattering intensity increases within the crystal position range of 180 mm to 255 mm as seen in Figure 4 (b), and size of oxygen precipitates can be assumed to increase.

[0042] However, although density of oxygen precipitates and oxygen layer breakdown voltage characteristics of MOS devices are known to appear strongly related, the relationship between crystal quality and the size of oxygen precipitates is still unclear.

[0043] The method of the present invention requires lowering of the rate of cooling over the 1150°C to 1000°C temperature range to 2.0°C/min. or below in order to lower density of oxygen precipitates across the wafer surface. The effect of the method of the present invention will be explained in detail below based upon working examples.

[0044]

[Working Examples] Silicon single crystal produced under the below mentioned conditions were used as samples. After wafer processing, the position of OSF ring generation following thermal oxidation was determined, and the density of oxygen precipitates observed at the wafer surface was measured by the infrared tomography method.

[0045] 1. Single Crystal Production Method: First 50 kg of high purity silicon single crystal was charged into a 16" diameter quartz crucible. Then after the polysilicon was melted by heating, a 150 mm diameter <100> crystal growth orientation single crystal was pulled to 1000 mm length.

[0046] 2. The crystal growth rate (fp) was set to 0.7 to 1.2 mm/min., and the temperature gradient (G) along the crystal axial direction over the crystal temperature range of the silicon melting point to 1300°C was set to 2.6 to 3.5°C/mm, so that the coefficient expressed as fp/G was always at least 0.25 mm^2/°C · min.

[0047] 3. Four conditions were used for which cooling rate in the temperature range of 1150°C to 1000°C was 2.5 to 2.2 °C/min., 2.0 to 1.8 °C/min., 1.5 to 1.1 °C/min., and 1.0 to 0.7 °C/min.

[0048] Results measured for the above measured conditions are shown in Table 1.

[0049]

[Table 1]

Crystal no.	Coefficient [Fp/G] for melting pt. - 1300°C range (mm^2/°C · min.)	Cooling rate over 1150°C - 1000°C (°C/min.)	Generation position of OSF ring	Density of oxygen precipitates (cm^{-3})
1	0.30	* 2.5 - 2.2	generated at wafer perimeter edge	$1 - 2 \times 10^6$
2	0.26	2.0 - 1.8	ditto	$8 - 10 \times 10^6$
3	0.28	1.5 - 1.1	ditto	$4 - 6 \times 10^5$
4	0.26	1.0 - 0.7	ditto	$1 - 2 \times 10^5$

[0050] As is clear from Table 1, the position of generation of the OSF ring can be set to the wafer outermost perimeter and density of oxygen precipitates across the wafer surface can be kept at $10^5 cm^{-3}$ by production of silicon single crystal under the conditions stipulated by the present invention.

[0051]

[Results of the Invention] By the silicon single crystal production method of the present invention, density of oxygen precipitates across the wafer surface can be controlled, and oxide layer breakdown voltage characteristics can be lowered without the post-wafer-processing thermal oxidation generation of an OSF ring that impedes LSI manufacturing processing. Therefore it becomes possible to manufacture with high efficiency single crystal of excellent crystal quality.

[Simple Explanation of Figures]

[Figure 1] This drawing shows schematically the relationship between the melt and interface of a pulled single crystal.

[Figure 2] This figure shows the relationship between exterior diameter (mm) of the OSF ring generated in the wafer and crystal growth rate (fp = mm/min.).

[Figure 3] This figure shows the relationship between OSF ring exterior diameter (mm) and the coefficient (fp/G = mm^2/°C · min) relating growth rate (fp = mm/min.) and the temperature gradient (G

= °C/m) in the crystal axial direction in the high temperature range of the silicon melting point to 1300°C).

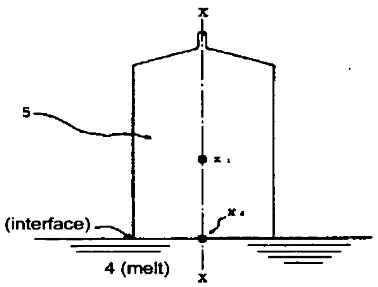
[Figure 4] This shows cooling rate and results of measurements by the infrared scattering tomography method; wherein (a) shows oxygen precipitate density, (b) shows square root of the scattering intensity of oxygen precipitates, and (c) shows the cooling rate over the temperature range of 1150°C to 1000°C.

[Figure 5] This is a schematic cross-sectional diagram showing conditions during the Czochralski method.

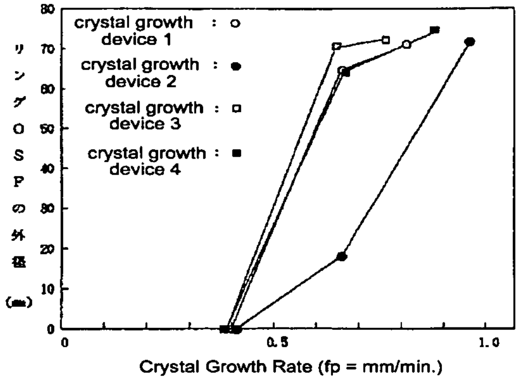
[Explanation of Items]

1 .... crucible
1a .... quartz vessel
1b .... graphite vessel
2 .... heater
3 .... seed crystal
4 .... melt
5 .... single crystal

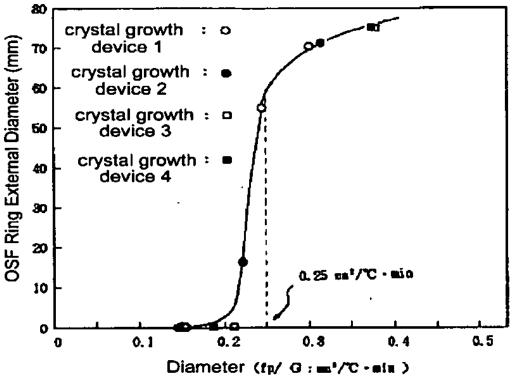
[Figure 1]



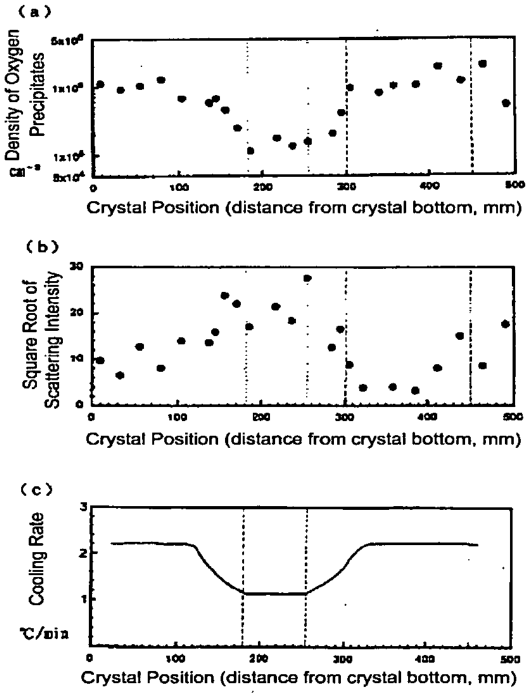
[Figure 2]



[Figure 3]



[Figure 4]



[Figure 5]